Proceedings of the Iowa Academy of Science

Volume 74 | Annual Issue Article 23

1967

The Movement of Chloride and Nitrate through Certain Iowa Soils

John C. Corey
Iowa State University

Don Kirkham
Iowa State University

Donald R. Nielsen
Iowa State University

The Movement of Chloride and Nitrate through Certain Iowa Soils[1]

JOHN C. COREY, DON KIRKHAM, AND DONALD R. NIELSEN

Abstract. Miscible displacement experiments were conducted to determine the influence of soil type on the movement of chloride and nitrate. The movement of NO_3^- is important in plant nutrition; Cl^-, in soil salinity. In these experiments, 100 ml of an aqueous solution containing 0.55 g of $CaCl_2$ and 0.35 g of $Ca(NO_3)_2 \cdot 4H_2O$ was displaced through 30-cm long soil columns with 0.01N $CaSO_4$. Breakthrough curves, plots of the chloride or nitrate concentrations found in the effluent against the volume of effluent collected, were made.

Breakthrough curves from columns of Webster, Ida, and Edina surface soils and a muck soil indicated that the velocity of chloride was greater than that of nitrate during displacement through these soils. On the other hand, breakthrough curves obtained from columns of Webster, Ida, Edina, and Clarion subsoils showed no separation of chloride and nitrate. The breakthrough curves for all soils studied differed in shape. The dispersion coefficient for chloride, calculated from the breakthrough curves, varied from 1.533 cm^2/hr for the muck soil to 0.094 cm^2/hr for the Ida, C horizon, soil. The experimentally determined dispersion coefficients were used to calculate theoretical chloride distributions for the muck, Ida, and Webster soils.

The movement of nitrate through soils is important in agronomic as well as in pollution studies. Agriculturalists are concerned with the movement of nitrate within the root zone of plants, while health authorities are concerned with the contamination of water supplies with nitrates from sources such as feed lots, fertilizer applications, and decaying organic matter. The movement of nitrate through soils is dependent on soil type, water content, velocity of flow, denitrification and nitrate immobilization. Chloride, since it is not normally present in soils of the humid region and is not decomposed or immobilized, is often used as a tracer of nitrate movement in field experiments (Wetselaar, 1961; Robinson and Gacoka, 1962; and Stephens, 1962). A comparison of the distribution of chloride with the distribution of nitrate has been used to evaluate the mineralization or denitrification that occurs to added nitrate. Unfortunately, careful evaluation of the relative displacement velocities of chloride and nitrate through the soils under study have not been made before the field experiments.

Investigators (Taylor, 1953; Rifai *et al.*, 1956) have used the solution of the following differential equation to describe the

[1] Journal Paper No. J-5381 of the Iowa Agricultural and Home Economics Experiment Station, Ames, Iowa. Project 998. Work supported by the U. S. Atomic Energy Commission, Contract No. AT-(11-1)-1260. The third author acknowledges support of a Senior Post-Doctoral National Science Foundation Fellowship.

concentration of a compound at different times and distances along a column of porous material; where c

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

is the concentration of the solute; t, time; x, the distance along the column; and D, the coefficient of dispersion analogous to a molecular diffusion coefficient. A solution to this differential equation, if we assume a constant average pore-water velocity v and no interaction of the compound with the soil is,

$$\frac{c}{c_0} = N\left(\frac{x + x_0 - vt}{\sqrt{2Dt}}\right) - N\left(\frac{x - vt}{\sqrt{2Dt}}\right) \tag{2}$$

for the conditions

$$\begin{array}{lll} c = 0 & x \geqq 0 & t = 0 \\ c = c_0 & x = 0 & 0 < t < t_0 \\ c = 0 & x = 0 & t \geqq t_0 \\ c = 0 & x \rightarrow \infty & t > 0 \end{array}$$

where x_0 is the length of column that the compound of concentration c_0 will occupy if no mixing occurred, t_0 (not explicit in equation 2) is the time for the fluid to travel a distance x_0 in the column, and N(x) is the normal probability integral

$$N(x) = [1/(2\pi)^{1/2}] \int_0^x e^{-x^2/2} dx$$

An experimenter can obtain all the values required in Equation 2, except the dispersion coefficient, from breakthrough curves (breakthrough curves are plots of the concentration of the compound found in the effluent against the volume of effluent collected) and a knowledge of the physical condition of the column. Hence, the experimenter can solve Equation 2 for D. Gardner (1965) used this equation to fit the data on nitrate movement in the field collected by Wetselaar (1962). In our work, we were interested in obtaining values of the dispersion coefficient for chloride for some Iowa soils. These dispersion coefficients can be used to predict the concentration of chloride in a soil profile after different quantities of water have been used to displace the chloride through saturated soil. We were also interested in evaluating the use of chloride to predict the movement of nitrate through these same soils.

Procedure

Miscible displacement experiments, using the experimental design of Nielsen and Biggar (1962), were conducted to determine the manner in which chloride and nitrate moved through different soils. Briefly, the design involved the sealing of plexiglas cylinders, 7.62 cm in diameter and 30 cm in length, with Marine resin to input end-plates and then packing the cylinders with airdry soil. The soil, before being packed in the columns, had been passed through a sieve with 2 mm square openings. The columns were water-saturated with 0.01N $CaSO_4$. The ion $Ca{++}$ is normally in soil water; it prevents soil particles from dispersing. The calcium sulfate solution was introduced into the columns from a reservoir behind the fritted glass-bead plate located in the plexiglas end-plate. After the soil was water-saturated, an end-plate at the effluent end was sealed in position. This end-plate, like the input end-plate, had a reservoir and a fritted glass-bead porous plate.

In these experiments, we brought the soil columns to steady-state flow conditions with 0.01N $CaSO_4$. Then, we added 100 ml of an aqueous solution of calcium nitrate and calcium chloride to the column. We displaced these 100 ml by the 0.01N $CaSO_4$. Finally, we analyzed the effluent solution for NO_3^- and Cl^- and plotted the concentration ratios, c/c_0, for these ions versus volume of effluent to obtain breakthrough curves. The solution containing the chloride and nitrate was made by adding 0.55 g of $CaCl_2$ and 0.35 g of $Ca(NO_3)_2 \cdot 4H_2O$ to a 100-ml flask and diluting to 100 ml with distilled water. The effluents from the water-saturated soil columns were collected with a fraction collector, consisting of a turntable with test tubes (Fig. 1). This figure also shows other parts of the experimental apparatus. The nitrate concentrations were determined by the methods of Bremner and Keeney (1965) and the chloride concentrations were determined by the Mohr method (Fischer, 1957).

The soils studied were the Clarion (A, B, and C horizons), Webster (A and B horizons), Edina (A_1 and A_2 horizons), Ida

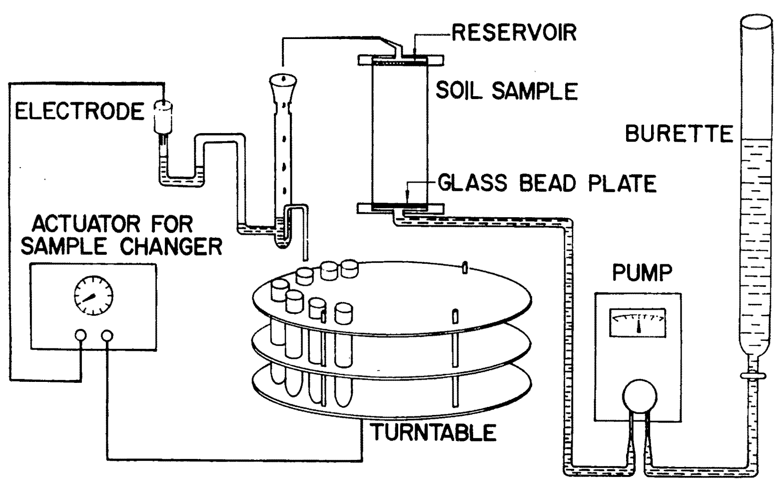

Figure 1. Experimental equipment for miscible displacement experiments.

(A and C horizons), and muck from the Colo bog. The Clarion, Webster, Edina, and Ida soils have been described by Oschwald *et al.* (1965); the muck has been described by Walker (1965). Chemical and physical properties of these soils are presented in Table 1. The clay content of these soils ranged from 21.6 to 41.6%. The organic carbon contents of the soil ranged from 0.17 to 27.12%. Physical properties of the soils were determined by standard methods.

Table 1. Chemical and physical properties of the soils used in the miscible displacement experiments.

Soil	Horizon	Texture[a]	Sand %	Silt %	Clay %	pH	Organic carbon %	Total nitrogen %
Ida	A	sicl	12.6	59.8	27.6	6.58	2.63	0.281
Ida	C	sil	27.0	51.4	21.6	7.50	0.21	0.021
Clarion	A	cl	46.8	25.4	27.8	5.50	1.71	0.142
Clarion	B	scl	56.8	15.8	27.4	5.50	0.50	0.046
Clarion	C	scl	56.6	19.8	23.6	7.80	0.17	0.017
Webster	A	cl	37.0	26.4	36.6	5.90	2.01	0.165
Webster	B	scl	48.8	21.8	29.4	7.25	0.31	0.037
Edina	A_1	sicl	15.2	49.2	35.6	5.10	3.05	0.237
Edina	A_2	sic	8.4	50.0	41.6	4.20	0.97	0.084
Muck	surface	..	..	...	....	6.20	27.12	2.040

[a] sicl, silty clay loam; sil, silt loam; cl, clay loam; scl, sandy clay loam; sic, silty clay

Theoretical distributions of ion concentrations for chloride in soil profiles were computed and graphed using experimentally determined values of dispersion coefficients and Equation 2.

Results

Results of the physical determinations of the soils are presented in the first six horizontal entries in Tables 2, 3 and 4. These tables also present other pertinent information about the experiments. The breakthrough curves obtained for the chloride and nitrate, after a solution of these ions had passed through the cylindrical columns 30 cm in length, are presented in figures.

Figure 2 shows the breakthrough curves for the columns of soil from the Clarion, A, B and C horizons. One concludes from the figure, since the data points for the chloride and nitrate each fall on the same curve, that the average velocity of the chloride and nitrate through the soils is the same. Figure 3, left, is for the Webster A horizon; the data points, unlike those of the preceding figure, do not fall on the same curve; instead, the data points for the chloride are displaced to the left; hence, we conclude that chloride moves faster than the nitrate in the soil of the Webster A horizon. Figure 3, right, is for the Webster B horizon. For it, the data points all lie on the same curve; hence, the velocities for

Table 2. Physical data for the miscible displacement experiments on Clarion soil (A, B, and C horizons); these data correspond to Figure 2.

Soil Horizon Sample texture	Clarion A clay loam	Clarion B sandy clay loam	Clarion C sandy clay loam
Bulk density (g/cm^3)	1.272	1.379	1.436
Bulk volume (cm^3)	1380	1380	1380
Pore space volume (cm^3)	631	583	569
Porosity (cm^3/cm^3)	0.457	0.422	0.412
Volume of H_20 in sample (ml)	631	583	569
Column length (cm)	30	30	30
Column cross sectional area (cm^2)	45.6	45.6	45.6
Column position	vertical	vertical	vertical
Hydraulic gradient (cm/cm)	2.17	1.50	4.42
Flow rate of effluent (ml/hr)	60	60	60
Velocity of flow (cm/hr)	1.32	1.32	1.32
Dispersion coefficient for chloride (cm^2/hr)	1.213	0.449	0.344

Table 3. Physical data for the miscible displacement experiments on Webster soil (A and B horizons) and muck from the Colo bog; these data correspond to Figures 3 and 4.

Soil Horizon Sample texture	Webster A clay loam	Webster B sandy clay loam	Muck surface
Bulk density (g/cm^3)	1.363	1.428	0.374
Bulk volume (cm^3)	1380	1380	1380
Pore space volume (cm^3)	573	573	1056
Porosity (cm^3/cm^3)	0.415	0.415	0.765
Volume of H_2O in sample (ml)	573	573	1056
Column length (cm)	30	30	30
Column cross sectional area (cm^2)	45.6	45.6	45.6
Column position	vertical	vertical	vertical
Hydraulic gradient (cm/cm)	15.67	12.20	5.50
Flow rate of effluent (ml/hr)	60	60	60
Velocity of flow (cm/hr)	1.32	1.32	1.32
Dispersion coefficient for chloride (cm^2/hr)	0.203	0.534	1.533

Table 4. Physical data for the miscible displacement experiments on Ida soil (A and C horizons) and on Edina soil (A_1 and A_2 horizons); these data correspond to Figures 5 and 6.

Soil Horizon Sample texture	Ida A silty clay loam	Ida C silt loam	Edina A_1 silty clay loam	Edina A_2 silty clay
Bulk density (g/cm^3	1.178	1.295	1.098	1.295
Bulk volume (cm^3)	1380	1380	1380	1380
Pore space volume (cm^3)	695	652	709	660
Porosity (cm^3/cm^3)	0.504	0.472	0.514	0.478
Volume of H_20 in sample (ml)	695	652	709	660
Column length (cm)	30	30	30	30
Column cross sectional area (cm^2)	45.6	45.6	45.6	45.6
Column position	vertical	vertical	vertical	vertical
Hydraulic gradient (cm/cm)	11.71	6.77	4.37	26.67
Flow rate of effluent (ml/hr)	60	60	60	60
Velocity of flow (cm/hr)	1.32	1.32	1.32	1.32
Dispersion coefficient for chloride (cm^2/hr)	0.244	0.094	0.241	0.800

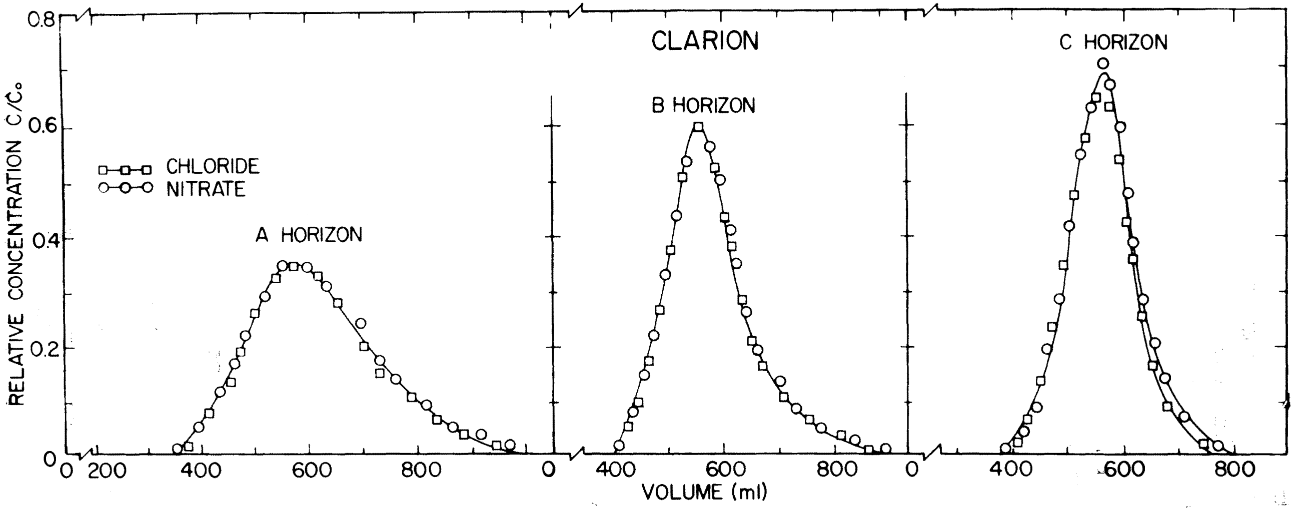

Figure 2. Breakthrough curves for a 100-ml aqueous solution of nitrate and chloride displaced through 30-cm long columns of soil from Clarion, A, B and C horizons; c is the concentration of the nitrate (or chloride) in the effluent, and c_0 is the concentration of the nitrate (or chloride) at the time the nitrate (or chloride) was introduced into the column; soil physical data are as in Table 2.

chloride and nitrate are the same. Figure 4 is for the muck and shows chloride moving through the soil faster than nitrate. Figure 5, left, is for the Ida A horizon and again shows the chloride moving faster than nitrate. Figure 5, right, is for the Ida C horizon and shows equal velocities of chloride and nitrate. Figure 6, left, is for the Edina A_1 horizon and shows a faster velocity for the chloride than for nitrate. Figure 6, right, is for the Edina A_2 horizon, and shows equal velocities for the chloride and nitrate.

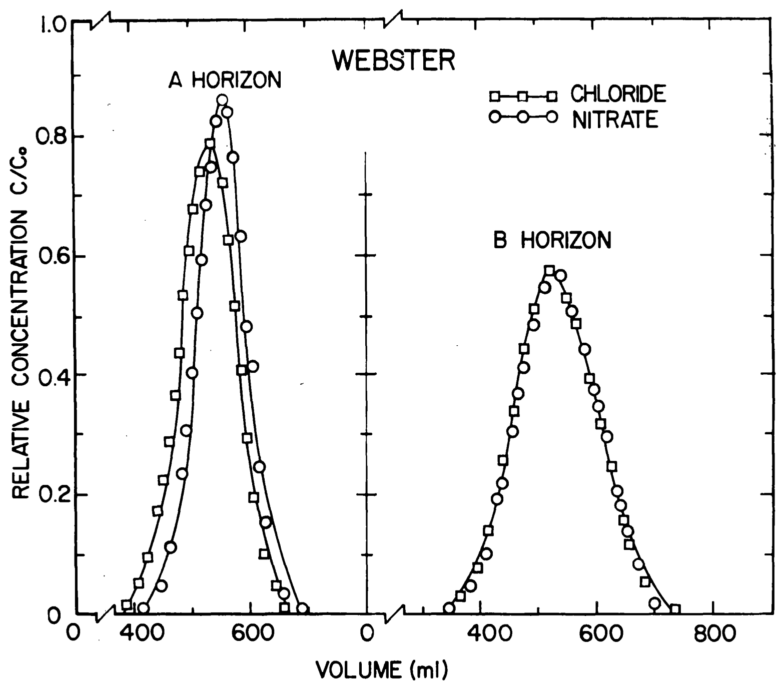

Figure 3. Same as Figure 2 except the soil is from Webster A and B horizons, Table 3.

Figure 7 is a different type of figure than 2-6. Figure 7 shows theoretical curves of chloride concentration ratio c/c_0 with depth for four different applications of water applied at the soil surface, 7.62, 15.24, 30.48 and (for the muck) 48.51 cm, when the columns of soil are Ida C horizon, Clarion A horizon, and muck. The curves are the c/c_0 condition that exists, with depth, at the instant when the last of these depths, 7.62 cm, 15.24 cm, etc., of the applied surface water has passed through the soil surface. To compute these curves, we used, in Equation 2, the values of dispersion coefficients, $D = 0.094$ cm^2/hr for the Ida C (see bottom line of Table 4); $D = 1.213$ cm^2/hr for the Clarion A (see

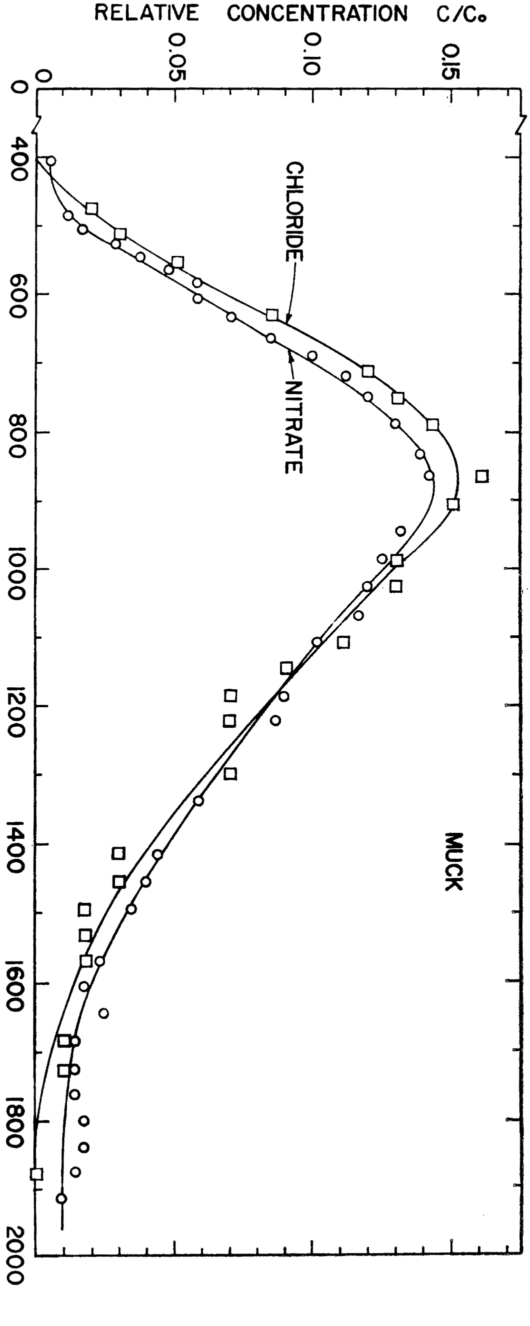

Figure 4. Same as Figure 2 except the soil is muck from the Colo bog, Table 3.

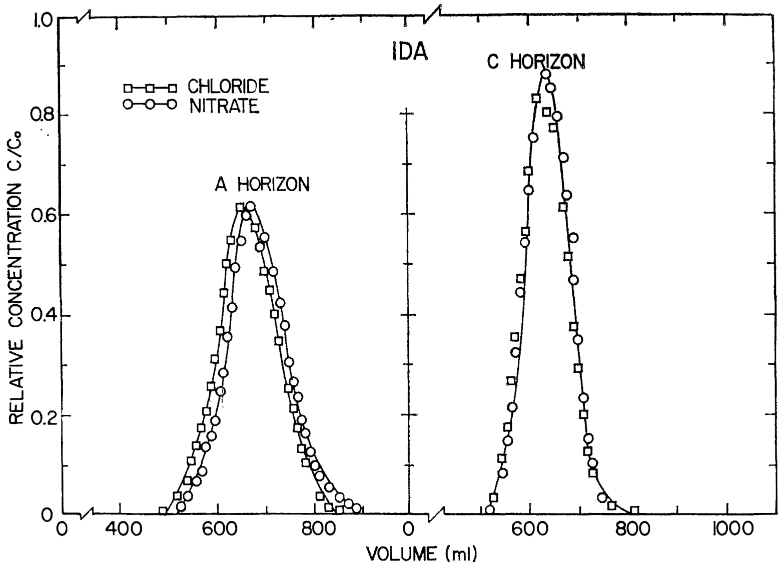

Figure 5. Same as Figure 2 except the soil is from Ida, A and C horizons, Table 4.

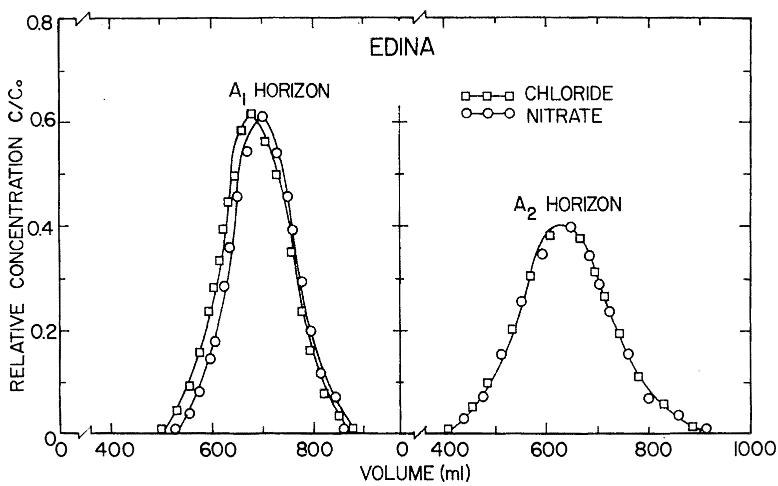

Figure 6. Same as Figure 2 except the soil is from Edina, A_1 and A_2 horizons, Table 4.

bottom line of Table 2); and D = 1.533 cm^2/hr for the muck (see bottom line of Table 3).

For all curves, we arbitrarily assumed that water entered the soil surface at 2 cm/hr so that velocity v of Equation 2 is 2 cm/hr divided by the porosity entry in Table 2, 3, or 4. For example, for Ida C, v = (2 cm/hr)/(0.472 cm^3/cm^3) = 4.24

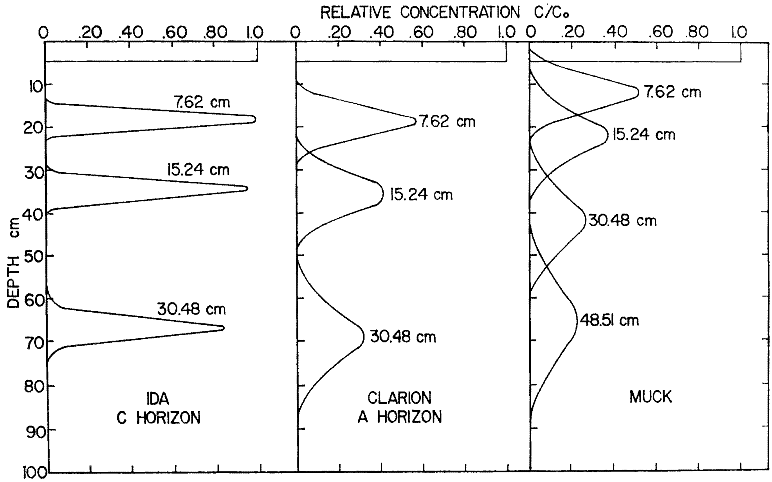

Figure 7. Theoretical distributions of chloride in an Ida C-horizon soil, a Clarion A-horizon, and a muck soil. When 7.62, 15.24, 30.48 and (for muck) 48.51 cm of surface water are applied, and the surface 4.7 cm of the soil has an initial chloride concentration ratio c/c_0 of one. The curves are shown for the instant that the last of the 7.62 cm, etc. of surface water has passed through the soil surface.

cm/hr. For each case in Figure 7, the chloride was assumed to be initially uniformly distributed in the top 4.7 cm of soil, as indicated by the rectangles of thickness 4.7 cm near the c/c_0 axes in the figure. In Figure 7, the calculations show the Ida C horizon peaks to be narrow. That is, there is little mixing of chloride in the soil as it moves through the column for the small, 0.094 cm^2/hr-dispersion coefficient. At the other extreme, the "peaks" of the muck curves are flat, showing much mixing for the large dispersion coefficient 1.533 cm^2/hr. Moreover, because the porosity for the muck is large (0.765 cm^3/cm^3) compared with Ida C (0.472 cm^3/cm^3), the concentration peaks are further reduced in height for the muck as compared with the Ida C.

Discussion

Although Wetselaar (1961), Stephens (1962), and Robinson and Gacoka (1962) concluded from their experiments that chloride and nitrate moved through the soil with the same velocity, we have found that one cannot generalize their finding to all soils and horizons, because (Fig. 2-6) the chloride and nitrate did not travel at the same velocity through the 30-cm long columns packed with Webster, Ida, or Edina soils from the A horizon, or through the columns of muck soil. The different velocities we believe depended on the relatively high organic-matter content of the surface horizons, because we found no velocity differences of the chloride and nitrate when they moved through subsoils, A_2, B and C horizons, where there is relatively little organic matter. The Clarion A where the velocity differences were small also had little organic matter. We conclude that chloride may be used as a tracer of nitrate for subsoils low in organic matter, but, since chloride does not move with the same velocity as nitrate through surface soil, we conclude that chloride ion is of questionable value as a tracer for nitrate in surface soils (containing organic matter). Other research workers commonly compare chloride and nitrate behavior in soils to assess microbial activity. Our work shows dispersion is an important factor.

The dispersion coefficients calculated for chloride varied widely for the various soils (Table 1). This observation would be expected because the soils had different textures. Also, some of the soils swelled; the aggregation status was different, and porosities and bulk densities (Tables 2, 3 and 4) were different.

Conclusions

1. Chloride and nitrate may not move at the same velocity through the same soil. Breakthrough curves obtained on soil from surface horizon Webster, Ida, and Edina showed that chloride was displaced through these soils at a faster velocity than was nitrate. On the other hand, chloride and nitrate were displaced at equal velocities through Clarion soil, A, B, and C horizons; through Edina soil, A_2 horizon; through Webster soil, B horizon; and through Ida, C horizon.
2. The shape of the breakthrough curves for chloride and nitrate varied greatly with soil type and horizon. Muck from the Colo bog had a wide breakthrough curve, while Ida C horizon had a narrow breakthrough curve; breakthrough curves for other soils were intermediate in shape.
3. Differences in quantities of chloride and nitrate moving through soil may not be ascribed completely to microbial activity; dispersion may be an important factor, especially in the presence of organic matter.

Literature Cited

Bremner, J. M. and Keeney, D. R. 1965. Analytica Chimica Acta 32:485-495.

Fischer, Robert B. 1957. Quantitative chemical analysis. W. B. Saunders Company. Philadelphia. 1-401.

Gardner, W. R. 1965. Soil Nitrogen, American Society of Agronomy Monograph No. 10:550-572.

Nielsen, D. R. and Biggar, J. W. 1962. Soil Science Soc. of America Proc. 26:216-221.

Oschwald, W. R., Riecken, F. F., Dideriksen, R. I., Scholtes, W. H., and Schaller, F. W. 1965. Iowa State University of Science and Technology Cooperative Extension Service Special Report 42.

Rifai, M. Nour Eddine, Kaufman, Warren J., and Todd, David K. 1956.

University of California (Berkeley), Division of Civil Engineering, Sanitary Engineering Research Laboratory Report 3.
Robinson, J. B. D. and Gacoka, P. 1962. Jour. of Soil Sci. 13:133-139.
Stephens, D. 1962. Jour. of Soil Sci. 13:52-59.
Taylor, Sir Geoffrey. 1953. Roy. Soc. London Proc., Series A, 219:186-203.
Walker, Patrick Hilton. 1965. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology.
Wetselaar, R. 1961. Plant and Soil 15:121-133.
——————, 1962. Plant and Soil 16:19-31.